Corrosion behavior and biocompatibility of additively manufactured 316L stainless steel in a physiological environment: the effect of citrate ions

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\section*{A R T I C L E  I N F O}

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Biocompatibility

\section*{A B S T R A C T}

In order to mitigate potential implant failures, it is essential to determine the corrosion behavior of biomaterials in a realistic physiological environment. In order to simulate the real oxidative nature of human body fluid, this research considers the effects of a complexing agent while determining the corrosion behavior of 316L stainless steel (SS) that has been fabricated by Selective Laser Melting (SLM) process. The results show that the complexing agent, i.e. the citrate ion, in Phosphate Buffer Saline (PBS) solution strongly affects the passivation behavior of 316L SS by complex species formation. However, due to a rapid solidification process, the microstructural properties of the additively manufactured metal are not similar to that of the conventionally manufactured counterpart. The microstructure of the SLM 316L SS contains refined sub-grains within each coarse grain and the formation of micro-inclusions i.e. MnS is restricted. The SLM 316L SS had better pitting resistance and passive film stability. \(E_{\text{corr}}\) for the SLM 316L SS was consistently higher and the breakdown potential, \(E_{\text{bd}}\), was more than three times higher compared to the wrought counterpart as determined by cyclic potentiodynamic polarization. Moreover, the SLM sample had a wider passive region and higher charge transfer resistance (\(R_t\)) (approximately 1.5 to 2.5 times) as determined by cyclic voltammetry and electrochemical impedance spectroscopy, respectively. In addition, the attachment and proliferation tendency of MC3T3-E1 pre-osteoblast cells were studied to evaluate biocompatibility. The SLM part had better cell proliferation. To summarize, in a physiological environment, the SLM 316L SS outperformed the conventional wrought 316L SS in terms of corrosion resistance and biocompatibility.

\section*{1. Introduction}

Additive Manufacturing (AM) is the latest trend in the manufacturing industry because of its inherent potential to fabricate near-net-shaped products with high intricacy and design flexibility. This layer-by-layer manufacturing technique allows building a three-dimensional (3D) object from a computer-generated design file without almost any geometrical constraint, which would be nearly impossible to achieve with conventional manufacturing processes. Among several additive manufacturing techniques [1,2], Selective Laser Melting (SLM) is a widely used manufacturing process for industrial applications, which is based on powder bed fusion [3].

The selection of process parameters is of prime importance to suppress different types of defects associated with the SLM technique, such as porosity, incomplete fusion holes, and cracks [4]. Numerous studies have been performed to correlate the SLM process parameters and the microstructure of the fabricated part [5–11]. In the SLM process, the material encounters fast local melting and cooling (cooling rate \(\sim 10^2\)–\(10^7\) K/s) due to a high-temperature gradient (\(\sim 10^9\) K/m) [10,12]. Due to the complex thermal cycle associated with the SLM technique, the microstructure of the fabricated part differs significantly from a conventionally manufactured part, and consequently, the surface and bulk properties also vary [8,11,13]. For example, separate studies by Sun et al. [14] and Wang et al. [15] have revealed that by the collective effects of hierarchically heterogeneous microstructures, such as cellular solidification, high angle grain boundaries, and dislocations as well as by tailoring certain crystallographic textures, it is possible to overcome the long-standing stress-ductility dilemma of metallic engineering materials through the SLM process. Several studies have also been performed on the corrosion performance of SLM parts and it has been found that SLM parts outperformed the conventionally manufactured parts in terms of corrosion resistance when process parameters were

\(E_{\text{corr}}\) \(E_{\text{bd}}\) \(R_t\) MC3T3-E1
selected appropriately [16–21]. Due to the inherent versatility of design and superior performance of SLM parts, this additive manufacturing technique is extensively used in aerospace, automotive, and biomedical applications [22]. Through the SLM process, it is also possible to fabricate functionally graded next-generation bio-implantable parts with lower stiffness to mitigate stress shielding effects and improve bone regeneration [23].

316L stainless steel (SS) has been used for a long period as a metallic biomaterial for orthopedic implants to make artificial joints, bone plates, screws, and nails due to its reliable combination of biocompatibility, excellent mechanical properties, reasonable corrosion resistance, and cost [24]. However, one of the major limitations of 316L SS as an implant material is its susceptibility to localized corrosion. More than 90% of the failures of 316L SS implants is the result of localized corrosion [25]. In-vitro studies of the corrosion performance of metallic bioimplant materials have been performed in simulated body fluid environments such as PBS solution, Hank’s solution or Ringer’s solution [25]. In reality, these solutions cannot entirely simulate the physiological environment of the human body, which contains different complexing (chelating) agents and proteins. Despite having a thin protective passive film, which is mainly composed of iron and chromium oxides or hydroxides, stainless steel is strongly affected by the presence of complexing agents or proteins [26,27]. Complexing agents or proteins are capable of binding metal ions released from the implant surface to form complex molecules [28]. These complex species may either cluster together surrounding the tissues of metallic implant or be transported to different parts of the body through the bloodstream. As a result of complex species formation, the passivation mechanism of stainless steel in physiological environments is greatly affected [29,30].

Due to this fact, corrosion driven in-vitro materials degradation studies for bioimplants should include complexing agents to simulate a more realistic environment [31]. Although several studies on electrochemical performance of the selective laser melted 316L SS have been performed in simulated body fluid [17,20,32], to the best of author’s knowledge, the effects of complexing agents on SLM 316L SS in the physiological environment have yet to be elucidated.

Therefore, herein the electrochemical performance of SLM 316L SS is studied in PBS solution with and without the addition of citrate ions to investigate the effect(s) of complexing agents. Citrate is used as a proxy for species produced in the “citric acid cycle” [33,34], a carbohydrate metabolic process in the human body [35]. At lower pH values, citric acid is passivating in nature and does not provoke active metal dissolution. But in non-acidic biological environments, it can alter the metal dissolution mechanism by forming either soluble solution complexes or surface complexation. The latter can detach from the alloy surface leading to metal dissolution [36]. How the corrosion behavior of SLM 316L SS is affected by complexing agents in physiological environments is elucidated and compared with the performance of the wrought 316L SS.

Finally, another important criterion for desirability in bio-implantable materials is the integrity of the implant and surrounding host tissue interface. Osteoblast cell adhesion on the implant substrate is the primary demand for proper cell function and successful osseointegration. Poor osseointegration may lead to inflammation and loosening of the implant [37]. Biological response to SLM and wrought 316L SS alloys has also been performed to monitor the morphology and proliferation tendency of pre-osteoblast cells (MC3T3-E1) over a 48 hours incubation period.

2. Experimental

2.1. Materials

The selective laser melted austenitic 316L stainless steel samples were fabricated from gas-atomized AISI 316L SS powder supplied by Renishaw®. To avoid undesired porosity and interlayer inhomogeneity, it is recommended to use spherical particles with a narrow size distribution [38]. The powders used in this study possessed mostly spherical morphology with small satellites attached for a few particles (as shown in the inset of Fig. 1). The particle size distribution was in the range of 7 to 57 μm with a 95% confidence interval that the mean value of the particle size was within 26.09 to 27.44 μm. The 80th percentile (P80) of the particles was below 29.31 μm.

![Fig. 1. 316L SS powder particle size distribution and morphology (inset).](image-url)
2.2. Sample preparation

Samples were fabricated using a Renishaw AM250, an SLM system having a continuous wavelength (1060 nm) Ytterbium fiber laser with a beam spot size of 75 μm. The fabrication process parameters are reported in Table 1. The scanning speed (v), energy density (E), and fluence (F) were calculated using the following equations [6,39]:

\[
\text{Scanning speed} = \frac{\text{point distance}}{\text{exposure time}}
\]

\[
\text{Energy density} = \frac{\text{laser power}}{\text{scan speed} \times \text{hatch distance} \times \text{exposure time}}
\]

\[
\text{Fluence} = \frac{\text{laser power} \times \text{exposure time}}{\text{point distance} \times \text{hatch distance}}
\]

Circular disk-shaped samples (diameter 15.8 mm and thickness 5 mm) were fabricated in vertical build direction (the flat surface parallel to the XY plane of the build plate) and chessboard scanning strategy was employed with 5×5 mm² island size, as shown schematically in Fig. 2. Despite being a smaller-sized test sample, the chessboard scanning strategy was employed to homogenize the distribution of residual stress as much as possible. Before starting the scanning, the build plate was preheated to 170 °C. The build chamber was evacuated until the residual oxygen content was less than 0.1% and high purity argon was supplied to maintain an inert atmosphere and reduce any chance of oxidation. In order to reduce the high-temperature gradient and stress concentration in the bulk volume, the scanning direction of each layer was rotated 67° relative to the previous layer. After scanning each layer, the laser beam contoured the periphery twice. It is to be noted that during the SLM process, the up-skin, down-skin, and volume of the part were subjected to similar process parameters. Consequently, different cross-sections of the part throughout the build direction, i.e. cross-sections parallel to the XY plane (Fig. 2), possessed identical process parameters. Wrought 316L stainless steel (Purchased from OnlineMetals®) was used as a counterpart of the SLM produced 316L SS for comparison purposes. For electrochemical and cell adhesion studies, all samples were polished sequentially using 180 to 1200 grit size SiC papers, followed by thorough cleaning in ethanol in an ultrasonic bath. The samples were rinsed in deionized water, dried under N₂ stream and then used for further characterization.

2.3. Materials characterization

Elemental composition of SLM and wrought 316L SS was determined by Energy dispersive X-Ray spectroscopy (EDX) analysis using Hitachi S-3400-II scanning electron microscope (SEM) equipped with an EDX analyzer. A backscattered electron detector was used to obtain the near-surface composition. To investigate constitutional phases and crystallographic orientations, X-Ray Diffraction (XRD) patterns were acquired with a Rigaku Ultima IV Diffractometer using Cu Kα X-Ray target (1.5408 Å) at 40 kV and 44 nA within 2θ ranging from 20°-80° with a step size of 0.02° at a speed of 1°/min. Microstructural characterization was carried out with the Hitachi S-3400-II SEM. To obtain microstructural features, mechanically polished (up to 1200 grit SiC finish) samples were further mirror polished with a 1 μm diamond suspension on polishing cloth followed by chemical etching for 40 s in an etchant solution (42 ml) containing hydrochloric acid (37%, 15 ml), nitric acid (70%, 10 ml), acetic acid (99%, 15 ml), and glycerol (99.5%, 2 ml).

2.4. Electrochemical measurements

Electrochemical analysis of additively manufactured 316L SS and wrought 316L SS was performed with a Gamry Reference 1000E potentiostat in a three-electrode cell. For each experiment, a freshly polished (1200 grit SiC finish) test sample was prepared and used as a working electrode having an exposed surface area of 1 cm². A platinum

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**Table 1**

Optimized parameters of the SLM process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser power (W)</td>
<td>200</td>
</tr>
<tr>
<td>Hatch distance (μm)</td>
<td>70</td>
</tr>
<tr>
<td>Point distance (μm)</td>
<td>60</td>
</tr>
<tr>
<td>Exposure time (μs)</td>
<td>100</td>
</tr>
<tr>
<td>Layer thickness (μm)</td>
<td>50</td>
</tr>
<tr>
<td>Scanning speed (mm/s)</td>
<td>600</td>
</tr>
<tr>
<td>Energy density (J/mm³)</td>
<td>95.23</td>
</tr>
<tr>
<td>Fluence (J/mm²)</td>
<td>4.76</td>
</tr>
</tbody>
</table>

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Fig. 2. Schematic fabrication strategy of the SLM process.
coast was used as the counter electrode, while a saturated calomel electrode (SCE, +0.242 V vs. SHE) was used as the reference. All potentials were recorded at an ambient temperature of 22 ± 1 °C.

Experiments were performed in Phosphate Buffer Saline (PBS) with and without the addition of citrate buffer solution as a complexing agent. One PBS tablet (Sigma-Aldrich®) was dissolved in 100 ml of deionized water to prepare the PBS solution of pH 7.2 ± 0.01. The chemical composition of the PBS solution was 8 g/L NaCl, 0.3 g/L NaHCO3, 0.2 g/L MgSO4, 0.14 g/L CaCl2, 0.06 g/L KH2PO4, and 0.06 g/L Na2HPO4. The citrate buffer solution of pH 6 containing 0.05 M citrate was prepared by dissolving 6.022 g of sodium citrate dihydrate (Sigma-Aldrich®) and 0.868 g of citric acid salts (Acros organics®) into 500 ml of deionized water. After the addition of citrate buffer solution into the PBS, pH was adjusted to 7.2 ± 0.01 by dissolving anhydrous NaOH pellets (Acros organics®). Henceforth, this electrolyte will be referred to as “citrate-PBS”. Moreover, electrochemical tests were also performed in pure citrate buffer solution (pH 6). Additionally, to measure the effect of the citrate ion in the presence of only chloride ions, further experiments were performed with a total chloride concentration of 4.94 g/L (equivalent to PBS solution) in citrate buffersolution (pH 6.0) and after pH adjustment to 7.2.

Before all electrochemical experiments, the working electrode was kept at the open circuit potential (OCP) in the test electrolyte until the potential variation was below 0.3 mV/min (up to 2 hrs). Cyclic potential-tendiodynamic polarization (CPP) curves were obtained at a scan rate of 1 mV/s, commencing from −0.5 V (vs. OCP) until an apex potential of +1.5 V (vs. OCP), or until an apex current density (25 mA/cm²) was measured during anodic polarization, whichever came first. This was followed by reverse polarization to −0.2 V (vs. OCP) at the same scan rate (1 mV/s). Cyclic voltammograms (CV) were done at a scan rate of 50 mV/s. CV scans were started from −1.0 V (vs. SCE) in the anodic direction up to +1.0 V (vs. SCE) for the SLM 316L SS, while the scanning range for the wrought 316L SS was limited to +0.4 V (vs. SCE) due to significant increase of the current density beyond this potential. For the electrochemical impedance spectroscopy (EIS) experiments, the working electrode was subjected to an AC potential with an amplitude of ±5 mVpeak at OCP over a frequency range of 100 kHz to 10 mHz. The reproducibility and consistency of each experiment were monitored and ensured by repeating the experiments three times.

2.5. Cell proliferation tests

MC3T3-E1 pre-osteoblast cells were used to study the cell proliferation and attachment on both 316L SS samples. Cells were cultured in a controlled atmosphere (37 °C, 95% humidity, and 5% CO2) in an α-modified minimum essential medium, which contained 10% fetal bovine serum (ThermoScientific™) and 1% penicillin-streptomycin (Sigma-Aldrich®). 200 μL of cell medium accommodating 15000 cells (counted using a Countess II FL, Life Technologies) was placed into a well tube containing sterilized samples and incubated for 48 hours. After the incubation period, cell staining was performed using NucBlue® (Invitrogen Inc.) for nuclei and ActinRed™ 555 (ThermoFisher Scientific) for F-actin filaments of the cytoskeleton. An EVOS® FL Cell Imaging System (AMF4300, Invitrogen Inc.) was used for fluorescence imaging.

Table 2: Elemental composition of the 316L SS (in wt. %) samples used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>O</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
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<tr>
<td>Powder</td>
<td>16-18</td>
<td>10-14</td>
<td>2-3</td>
<td>≤2</td>
<td>≤1</td>
<td>≤0.05</td>
<td>≤0.1</td>
<td>≤0.06</td>
<td>≤0.045</td>
<td>≤0.03</td>
<td>Bal</td>
</tr>
<tr>
<td>SLM</td>
<td>17.45</td>
<td>11.24</td>
<td>2.17</td>
<td>1.39</td>
<td>0.57</td>
<td>0.03</td>
<td>0.06</td>
<td>0.07</td>
<td>0.02</td>
<td>0.02</td>
<td>Bal</td>
</tr>
<tr>
<td>Wrought</td>
<td>17.21</td>
<td>10.37</td>
<td>2.14</td>
<td>1.91</td>
<td>0.51</td>
<td>0.10</td>
<td>0.04</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>Bal</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Elemental composition and phase assembly

Chemical compositions of selective laser melted 316L SS and wrought 316L SS bulk samples gathered from EDX window scanning results are reported in Table 2 along with the powder 316L SS composition (provided by the manufacturer). In comparison to the powder composition, no significant change in the chemical composition of the SLM 316L SS was observed during the manufacturing process as evident in Table 2.

The pure austenitic phase of the gas-atomized 316L SS powder was confirmed by the XRD spectrum of the precursor powder (as shown in Fig. 3) with obvious crystallographic peaks from γ(111), γ(200), and γ(220) at 2θ 44.08°, 51.24°, and 75.08°, respectively. The bulk 316L SS, fabricated through the SLM process had similar crystallographic peaks originating from the same orientations confirming pure face-centered cubic (fcc) gamma (γ) austenite phase without the formation of any secondary ferrite peaks. Secondary delta (δ) ferrite sometimes may appear due to the scattering effect during the SLM process as a result of using recycled powder [40]. As fresh powder was used to fabricate the SLM samples, the resultant structure is free from the δ ferrite phase. It is obvious from the peak intensities that in case of the powder 316L SS, the highest diffraction at 44.08° corresponded to the (111) crystallographic plane, while the (220) preferential crystallographic orientation was observed for the SLM 316L SS at the selected set of fabrication process parameters. Thilis et al. [41] and Liverani et al. [5] reported that competitive crystallographic orientation is dictated by the scanning strategy employed during the fabrication process and build direction. Liverani et al. [5] observed that in the chessboard scanning strategy, samples built at 45° build direction prefer (111) crystallographic orientation, while samples built at 90° build direction (vertical build direction) prefer (220) plane. Moreover, Kong et al. [17] found that for lower laser power (120 W), crystallographic grains prefer the (111) orientation whereas at higher laser power (200 W) the preferential grain orientation shifts to the (220) direction. The XRD pattern of the SLM 316L SS sample in our study is consistent with their results. The XRD pattern of wrought 316L SS clearly shows the presence of a purely austenitic phase without showing any diffraction peaks associated with δ ferrite. The peaks of the SLM sample appeared to be slightly wider compared to the wrought counterpart. According to the Scherrer formula [42], the comparatively broader peaks of SLM parts might be the result of grain refinement.

3.2. Microstructure

Microstructural features of the SLM 316L SS are shown in Fig. 4a delineating the distinctive structure of the laser melting process compared to the wrought 316L SS. Each coarse grain contains colonies of cellular and columnar sub-grains (Fig. 4b) ranging from sub-micron to nanometer in size. The sub-granular columnar structure was formed at a high solidification rate intrinsic to the SLM process. Such heterogeneous microstructure was developed due to the complex and repetitive thermal excursions produced by the laser beam during the layer by layer melting process. Despite being subjected to equal laser energy density, the melt pool and heat-affected zone, i.e. the melt pool.
boundary, of the laser melting process experience non-linear cooling due to differences in temperature gradients. At the melt pool region, the cooling rate is high due to a high degree of convection heat transfer and a cellular microstructure is formed. The size of these polygonal-shaped equiaxed cellular sub-grains was found to be between 400 to 800 nm as evident in Fig. 4c and is consistent with other studies [13,43,44]. Near the melt pool boundary, the cooling rate is relatively lower and slightly coarser such that elongated cellular sub-grains are observed. Thus, the columnar grains may form during solidification and would grow in the direction of heat flow. A re-melting region is established due to overlapping of laser tracks in the subsequent scan lines and randomly distributed columnar grains would appear with directional solidification towards the maximum temperature gradient direction. However, no specific directional orientation of the grains can be defined in the entire microstructure due to complex inter-mixing of granular structures during the layer by layer fabrication process. It is believed that rotation of the scanning direction (67°) between each successive layer and sequential intersection of reverse and forward polarization scans is the protection potential (E_{corr}) for the wrought sample also results in rapid propagation and spreading of the initiated pits and is confirmed by pit morphology after CPP scans, as shown in Fig. 7. Higher number of pits were formed on the surface of the wrought sample compared to the SLM sample. The width of the largest pit formed on the wrought and SLM sample was approximately 105 μm and 74 μm, respectively. The intersection of reverse and forward polarization scans is the protection potential (E_{pp}). The higher E_{pp} (−67.0 ± 10.6 mV_{SCE}) of the SLM 316L SS compared to the wrought 316L SS (−204.3±12.5 mV_{SCE}) also demonstrates its low pitting susceptibility. The E_{pp} is the potential below which the passive film is stable and new pit initiation and propagation are restricted beyond this potential, only the pre-existing pits may grow if present on the surface [48]. To compare the pitting behavior of these samples and to avoid the effect of E_{corr} values, the pitting resistance (E_{pit} − E_{corr}) and passive film stability/pitting susceptibility resistance (E_{pp} − E_{corr}) were also determined and they are provided in Table 3. As a consequence of higher E_{pit} and E_{pp} values, one could expect better stability of the passive film on the SLM alloy. In PBS, the values of (E_{pit} − E_{corr}) and (E_{pp} − E_{corr}) for the SLM samples were 1393.0 ± 22.9 mV and 241.3 ± 23.0 mV, respectively, whereas, the corresponding values measured for the wrought samples were 347.3±13.8 mV and 241.3±23.0 mV, respectively, whereas, the corresponding values measured for the wrought samples were

3.3. Electrochemical behavior

3.3.1. Cyclic potentiodynamic polarization

In order to evaluate the localized corrosion susceptibility of SLM 316L SS and wrought 316L SS in a biological environment, cyclic potentiodynamic polarization (CPP) was performed in PBS with and without the addition of complexing agent, i.e. 0.05 M sodium citrate. The quantitative values of the electrochemical parameters extracted from the polarization curves (CPP scans) shown in Fig. 6 are listed in Table 3.

In PBS solution (Fig. 6a), the corrosion potential (E_{corr}) of SLM 316L SS is found to be slightly more positive (−308.3 ± 15.1 mV_{SCE}) than the wrought sample (−351.3 ± 11.4 mV_{SCE}) indicating a relatively lower corrosion susceptibility of the former in PBS solution. In support of this, the wrought sample had a higher corrosion current density (i_{corr} = 0.79 ± 0.05 μA/cm²) compared to the SLM (0.69 ± 0.04 μA/cm²). During anodic polarization, the relatively small anodic current density (1.97 ± 0.06 μA/cm²) beyond −250 mV_{SCE} (referred to as the passive current density; i_{pass}) of the SLM 316L sample compared to the wrought (2.26 ± 0.06 μA/cm²) sample, corresponds to the formation of a denser oxide film on the former’s surface [47]. The passive oxide film formed on the SLM 316L showed remarkable stability even at large anodic potential up to 1084.7 ± 9.3 mV_{SCE}, which is designated as the breakdown potential (E_{bd}). However, the wrought 316L had a low E_{bd} of 347.3 ± 13.8 mV_{SCE}, which is consistent with a more limited stability of the passive film. In the case of the wrought sample, the abrupt increase in the current (beyond E_{pass}) during the forward scan, into the transpassive region, clearly reflects the dissolution of the alloy. During the reverse scan, both samples had a positive hysteresis loop indicating pitting. The higher E_{pit} value of the SLM 316L is consistent with superior resistance to pitting. The larger hysteresis width (the difference between the passive current density and the maximum current density during the reverse scan) for the wrought sample also results in rapid propagation and spreading of the initiated pits and is confirmed by pit morphology after CPP scans, as shown in Fig. 7. Higher number of pits were formed on the surface of the wrought sample compared to the SLM sample. The width of the largest pit formed on the wrought and SLM sample was approximately 105 μm and 74 μm, respectively. The intersection of reverse and forward polarization scans is the protection potential (E_{pp}). The higher E_{pp} (−67.0 ± 10.6 mV_{SCE}) of the SLM 316L SS compared to the wrought 316L SS (−204.3±12.5 mV_{SCE}) also demonstrates its low pitting susceptibility. The E_{pp} is the potential below which the passive film is stable and new pit initiation and propagation are restricted beyond this potential, only the pre-existing pits may grow if present on the surface [48]. To compare the pitting behavior of these samples and to avoid the effect of E_{corr} values, the pitting resistance (E_{pit} − E_{corr}) and passive film stability/pitting susceptibility resistance (E_{pp} − E_{corr}) were also determined and they are provided in Table 3. As a consequence of higher E_{pit} and E_{pp} values, one could expect better stability of the passive film on the SLM alloy. In PBS, the values of (E_{pit} − E_{corr}) and (E_{pp} − E_{corr}) for the SLM samples were 1393.0 ± 22.9 mV and 241.3 ± 23.0 mV, respectively, whereas, the corresponding values measured for the wrought samples were
The improved corrosion behavior of SLM 316L SS compared to the wrought part can be explained by its passive film stability and pitting resistance parameters. The tendency to form a passive film and its attendant stability depend on various factors: electrolyte composition, pH, grain size, surface chemistry, the degree of impurity segregation, inclusions, and material processing method [49]. The stability of the passive film on the surface of SLM 316L SS can also be predicted from the uniform distribution of Cr across the inclusions as evaluated from EDS analysis (Fig. 5a and c). However, in the case of the wrought 316L SS, the depletion of Cr at the vicinity of inclusions (Fig. 5b and d) would disrupt the uniformity of the Cr-oxide passive film as evident in Fig. 6: this can be quantitatively observed from the lower values of \((E_{pp} - E_{corr})\) and \((E_{bd} - E_{corr})\). Several studies have also explained the effect of grain size on the corrosion behavior of metals [50–52]. These studies have mostly focused on a specific type of corrosion, i.e. inter-granular corrosion, pitting corrosion triggered by the impurity phases and/or due to grain refinement. For instance, Ralston et al. [53] and Gollapudi [54] emphasized that refined grain structure within a narrow grain size distribution range would encourage the formation of the compact passive film. In the case of the SLM 316L SS, each coarse grain is decorated with columnar and sub-grains that exist in colonies forming a micron and sub-micron polygonal cellular structure. This sub-grain structure facilitated the formation of a compact passive layer on the surface of SLM 316L SS (viz. the \((E_{pp} - E_{corr})\) and \((E_{bd} - E_{corr})\) values). Moreover, Li et al. [55] found that grain boundaries do not disturb chemical composition within the microstructure after grain refinement of stainless steel. Therefore, the combined effect of refined sub-grain structure and uniform distribution of Cr without micro-segregation facilitated the formation of a more compact passive oxide layer on the SLM 316L SS. The similar results on the improvement of passive film formation characteristics of SLM 316L SS in simulated body fluid have been reported by Man et al. [20]. Through Auger Electron Spectroscopy (AES) analysis, they found that the passive film formed on SLM 316L SS was relatively thicker compared to the wrought 316L SS because of the higher densities of sub-grain and grain boundaries of the former sample.

Halide ions, such as chlorides facilitate localized dissolution. It is widely accepted that MnS inclusions play a crucial role in the initiation of pitting by developing a Cr depleted zone surrounding the inclusion [56,57]. Once the chloride ions approach the Cr depletion region within the microstructure, it generates a localized acidic environment by hydrolysis, which further causes dissolution around the inclusion, initiating and propagating the pits [56]. In the case of wrought 316L SS, irregular shaped MnS inclusions and the associated Cr depleted region (as shown in Fig. 5b) prompt early pit initiation and propagation at a lower potential value. In contrast, the inherent high cooling rate of the SLM process is able to suppress MnS inclusion formation to a greater extent as a result of decreased \((10^5\) order of magnitude) diffusion time for Mn and S [16,20] and consequently avoid the development of the Cr depleted region (as shown in Fig. 5a). The absence of this localized Cr depleted regions within the microstructure of SLM 316L SS prevents early dissolution of the oxide layer even in the presence of chloride ions as evidenced by the very large overpotential required for passive film breakdown.

In the presence of 0.05 M sodium citrate in PBS, similar CPP trends are observed for both samples, as shown in Fig. 6b. With the addition of citrate ions, the \(E_{corr}\) values have shifted in the cathodic direction for both the wrought and SLM 316L SS. Higher \(i_{corr}\) and \(i_{pass}\) values are also observed by these samples in PBS containing citrate ions, which implies...
a detrimental effect from these species. Comparatively, in the presence of citrate ions, the $i_{\text{corr}}$ and $i_{\text{pass}}$ of the wrought sample were slightly ($i_{\text{corr, wrought}} = 1.16 \pm 0.04 \mu\text{A/cm}^2$ and $i_{\text{pass, wrought}} = 2.71 \pm 0.06 \mu\text{A/cm}^2$) higher than for the SLM 316L SS ($i_{\text{corr, SLM}} = 1.07 \pm 0.03 \mu\text{A/cm}^2$ and $i_{\text{pass, SLM}} = 2.65 \pm 0.04 \mu\text{A/cm}^2$). Moreover, the $E_{\text{corr}}$ of the wrought 316L SS has shifted to a more negative value ($E_{\text{corr, wrought}} = -520.7 \pm 23.0 \text{ mV SCE}$ and $E_{\text{corr, SLM}} = -428.4 \pm 12.9 \text{ mV SCE}$) in the presence of citrate ions compared to its $E_{\text{corr}}$ in pure PBS ($E_{\text{corr, wrought}} = -351.3 \pm 11.4 \text{ mV SCE}$ and $E_{\text{corr, SLM}} = -308.3 \pm 15.1 \text{ mV SCE}$). On the other hand, the effect of citrate ions on the shift of $E_{\text{ad}}$ for both samples is found to be negligible as given in Table 3.

Cyclic potentiodynamic polarization experiments were carried out in pure citrate buffer solution of pH 6, and the corresponding results for the SLM and wrought 316L SS are shown in Fig. 8. The SLM sample in pure citrate buffer solution had a similar $E_{\text{corr}}$ to the value measured in the citrate-PBS solution. For the wrought sample, a slightly higher $E_{\text{corr}}$ value is found in pure citrate buffer solution compared to citrate-PBS. A noticeable decrease of $i_{\text{corr}}$ is observed in pure citrate buffer solution for both test samples. Upon Cl$^-$ addition (at an equivalent amount to that used in PBS solution) to the citrate buffer solution (pH 6), the $E_{\text{corr}}$ values decreased slightly and $i_{\text{corr}}$ values increased remarkably for materials. A similar trend was noticed when CPP was carried out in Cl$^-$ containing citrate buffer solution after adjusting the pH value to 7.2. The quantitative values of $E_{\text{corr}}$ and $i_{\text{corr}}$ in Cl$^-$ containing citrate buffer solution (pH 7.2) are very close to the corresponding values in citrate-PBS solution. These results highlight the larger contributions of Cl$^-$ and
citrate ions to the electrochemical dissolution of stainless steel in the absence of phosphate-based buffering species. In other words, Cl– and citrate species at relatively low pH compared to the PBS solution (pH 7.2 vs. 6) significantly influence the corrosion behavior of stainless steel.

The interaction of H$_2$PO$_4^–$/ HPO$_4^{–2}$ species with the passive oxide film already present on the surface could inhibit its dissolution even in the presence of Cl– [58]. Similarly, it is expected that in the human body at the interface of an implant and its surrounding tissues, the decrease in local pH could adversely affect the barrier characteristics of the passive film. As shown in Fig. 8a, the SLM 316L SS was readily passivated in citrate + Cl– solution at both pH (6 and 7.2) above −250 mV$\text{SCE}$. However, in citrate buffer solution without Cl–, the gradual increase in the current during anodic polarization indicated a delay in the formation of a uniform passive film on SLM 316L SS. This behavior is attributed to the deleterious effect of citrate ions on the passive film formation/stability. During reverse polarization, the effect of Cl– ions on the passive film is found to be negligible at pH 6 and the presentation of negative loops corresponds to a low tendency for pitting. In contrast, the increase in current at approximately 930.4 ± 22.5 mV$\text{SCE}$ highlights the breakdown of the passive film at pH 7.2 (in Citrate + Cl– solution). The formation of a positive loop at pH 7.2 is consistent with the greater pitting tendency of SLM 316L SS at this pH. This behavior also suggests that the stability of the passive film and its tendency to pit are highly sensitive to the pH of the solution.

On the other hand, the passivation behavior of the wrought 316L SS sample was strongly affected by the Cl– ions and the polarization trends were independent of the change in pH of the electrolyte. For instance, the wrought 316L SS had similar anodic polarization trends in citrate + Cl– solution at both pHs (6 and 7.2). Similarly, the relatively large $i_{\text{pass}}$ and lower $E_{\text{corr}}$ of wrought 316L SS in the presence of Cl– compared to the values registered by the same sample in only citrate buffer solution (at pH 6 without Cl– addition) confirmed the decrease in passive film stability and improved pitting tendency. As given in Table 3, the pitting resistance and passive film stability of the wrought 316L SS decreased from 881.0 ± 32.2 mV to 809.3 ± 8.1 mV and from 419.0 ± 26.7 mV to 322.3 ± 5.0 mV, respectively, in the presence of Cl– ions in the citrate solution at pH 7.2. In other words, the SLM 316L SS had almost 1.5 times higher pitting resistance under applied conditions compared to the wrought 316L SS regardless of the presence of Cl– ions in the citrate solution.

The relatively large pitting resistance and passive film stability of SLM 316L SS make it a possible candidate to replace existing wrought 316L SS implants/biomedical devices. The approximately 100 mV lower pitting resistance and significantly lower passive film stability (334.0 ± 8.5 mV) of SLM 316L at the controlled pH of 7.2 in citrate + Cl– solution, compared to the values observed at pH 6 (with and without Cl– addition), highlight the marginal influence of Cl– but the important sensitivity towards pH changes.

The PBS solution contains an equivalent amount of Cl–. However, both 316L SS samples have a relatively lower corrosion rate in PBS compared to the citrate-containing PBS solution. This confirms the enhanced dissolution of Fe and Cr oxides/hydroxides in the presence of citrate ions that form stable complexed Fe and Cr species [29,36].

### 3.3.2. Cyclic voltammetry

Cyclic voltammetry (CV) was performed to investigate the interaction of ionic species i.e. Cl– and citrate in the PBS solution with the surface of both SLM and wrought 316L SS. Current response as a function of applied potential and current peak positions, can indicate the occurrence of reactions and help to identify a dissolution mechanism. For example, a cyclic potential sweep in the anodic direction

---

**Table 3**

T:10m CPP curves (n = 3) at a scan rate of 1 mV/s.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Sample</th>
<th>$E_{\text{corr}}$ mV$\text{SCE}$</th>
<th>$i_{\text{corr}}$ μA/cm$^2$</th>
<th>$i_{\text{pass}}$ μA/cm$^2$</th>
<th>$E_{\text{pit}}$ mV$\text{SCE}$</th>
<th>$E_{\text{pp}}$ mV$\text{SCE}$</th>
<th>$E_{\text{pit}}–E_{\text{corr}}$ mV</th>
<th>$E_{\text{pp}}–E_{\text{corr}}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>SLM</td>
<td>$-308.3 \pm 15.1$</td>
<td>$0.69 \pm 0.04$</td>
<td>$1.97 \pm 0.06$</td>
<td>$1084.7 \pm 9.3$</td>
<td>$-67.0 \pm 10.6$</td>
<td>$1393.0 \pm 22.9$</td>
<td>$241.3 \pm 23.0$</td>
</tr>
<tr>
<td>(pH 7.2)</td>
<td>wrought</td>
<td>$-351.3 \pm 11.4$</td>
<td>$0.79 \pm 0.05$</td>
<td>$2.26 \pm 0.06$</td>
<td>$347.3 \pm 13.8$</td>
<td>$-204.3 \pm 12.5$</td>
<td>$698.7 \pm 11.8$</td>
<td>$147.0 \pm 7.8$</td>
</tr>
<tr>
<td>Citrate–PBS</td>
<td>SLM</td>
<td>$-428.4 \pm 12.9$</td>
<td>$1.07 \pm 0.03$</td>
<td>$2.65 \pm 0.04$</td>
<td>$1093.3 \pm 8.3$</td>
<td>$-64.3 \pm 8.7$</td>
<td>$1521.6 \pm 11.6$</td>
<td>$364 \pm 20.8$</td>
</tr>
<tr>
<td>(pH 7.2)</td>
<td>wrought</td>
<td>$-520.7 \pm 23.0$</td>
<td>$1.16 \pm 0.04$</td>
<td>$2.71 \pm 0.06$</td>
<td>$328.4 \pm 16.2$</td>
<td>$-177.0 \pm 12.3$</td>
<td>$849.0 \pm 8.7$</td>
<td>$343.7 \pm 34.7$</td>
</tr>
<tr>
<td>Pure citrate buffer (pH 6)</td>
<td>SLM</td>
<td>$-435.0 \pm 10.5$</td>
<td>$0.21 \pm 0.03$</td>
<td>$1.52 \pm 0.05$</td>
<td>$1006.7 \pm 13.2$</td>
<td>–</td>
<td>$1441.7 \pm 6.8$</td>
<td>–</td>
</tr>
<tr>
<td>Citrate + Cl– (pH 6)</td>
<td>wrought</td>
<td>$-473.3 \pm 19.1$</td>
<td>$0.30 \pm 0.04$</td>
<td>$1.62 \pm 0.04$</td>
<td>$407.6 \pm 14.2$</td>
<td>$-54.0 \pm 8.5$</td>
<td>$881.0 \pm 32.2$</td>
<td>$419.0 \pm 26.7$</td>
</tr>
<tr>
<td>Citrate + Cl– (pH 7.2)</td>
<td>SLM</td>
<td>$-445.0 \pm 12.1$</td>
<td>$0.91 \pm 0.03$</td>
<td>$2.68 \pm 0.06$</td>
<td>$1015.0 \pm 8.2$</td>
<td>–</td>
<td>$1460.0 \pm 19.1$</td>
<td>–</td>
</tr>
<tr>
<td>Citrate + Cl– (pH 7.2)</td>
<td>wrought</td>
<td>$-503.7 \pm 15.0$</td>
<td>$0.92 \pm 0.02$</td>
<td>$2.89 \pm 0.05$</td>
<td>$308.3 \pm 15.9$</td>
<td>$-113.0 \pm 14.2$</td>
<td>$812.0 \pm 30.8$</td>
<td>$390.6 \pm 4.0$</td>
</tr>
<tr>
<td>Citrate buffer (pH 7.2)</td>
<td>wrought</td>
<td>$-504.0 \pm 9.8$</td>
<td>$1.11 \pm 0.03$</td>
<td>$2.87 \pm 0.05$</td>
<td>$305.3 \pm 13.8$</td>
<td>$-181.7 \pm 7.8$</td>
<td>$809.3 \pm 8.1$</td>
<td>$322.3 \pm 5.0$</td>
</tr>
</tbody>
</table>

---

Fig. 7. Pit morphology after CPP scan on (a) SLM 316L SS, (b) wrought 316L SS.
might identify oxidation peaks that can be associated with a given reaction. The voltammograms acquired for SLM 316L SS and wrought 316L SS in both PBS and citrate-PBS solutions are shown in Fig. 9. During the CV scan of SLM 316L SS, two anodic peaks (A1 and A2) and two cathodic peaks (C1 and C2) were identified irrespective of the electrolyte composition (Fig. 9a). When potential was swept (at 50 mV/s) from −1.0 V (vs. SCE) to positive potential, the transition from active dissolution to passivation of the surface initiated at the anodic peak (A1). The gradual increase in current prior to peak A1 is associated with oxidation of Fe to Fe(OH)2 species according to reaction 1 [29]. As observed from the CV scans, the anodic (A1) and cathodic (C1) peaks of both SLM and wrought 316L SS in PBS solution appear at almost the same potentials (−0.25 V and −0.5 V vs. SCE, respectively) that are possibly related to the (FeII/FeIII redox reaction i.e. oxidation of Fe(OH)2 to Fe(OH)3) via reaction 2 under applied conditions. In other words, the oxidation of Fe(OH)2 to Fe(OH)3 occurs at −0.25 V vs. SCE (peak A1) during anodic scan. Within this potential region (between peak A1 and A2), there exists Cr(OH)2+ species on the surface of both samples. In the PBS solution (at pH 7.2), the HPO42− species may also interact with this species according to reaction 3 and could further enhance the stability of the passive film.

\[
\begin{align*}
Fe + 2H_2O & \leftrightarrow Fe(OH)_2 + 2H^+ + 2e^- \quad (1) \\
Fe(OH)_2 + H_2O & \leftrightarrow Fe(OH)_3 + H^+ + e^- \quad (2) \\
Cr(OH)_2^+ + HPO_4^{2-} & \leftrightarrow CrOHPO_4^{+} + H_2O \quad (3)
\end{align*}
\]

Within the passive region, the film is composed of both Fe and Cr oxides/hydroxides at a potential higher than −0.25 V vs. SCE (peak A1). The Fe(OH)3 may possibly interact with the Cl− ions to form a coordination complex via reaction 4. This reaction is kinetically slow at such low potentials and pH (7.2) [59].

\[
Fe(OH)_3 + Cl^- \leftrightarrow Fe(OH)Cl^+ + 2OH^- \quad (4)
\]

In comparison, cyclic voltammograms of the wrought 316L SS exhibit one anodic peak (A2) and cathodic peak (C1) within the potential limit from −1.0 V to 0.4 V (vs. SCE) as shown in Fig. 9b. Peak A2 is not observed on the wrought 316L SS samples, possibly due to the depletion of Cr(OH)3 at the vicinity of surface defects such as Mn/S enriched non-metallic inclusions as noted in Fig. 5b. Just beyond 0.4 V (vs. SCE), the passive film completely breaks down resulting in a significant increase of current density (as shown in Fig. 9b inset). This is associated with pit formation on the surface. For this reason, the voltammetric scan was limited to a maximum potential of 0.4 V (vs. SCE) for the wrought samples. In the PBS solution, A1 and C1 appear at ∼−225 mV and ∼−500 mV (vs. SCE), respectively. In the case of a citrate-PBS solution, the corresponding peaks appear at ∼295 mV and ∼395 mV (vs. SCE), respectively. Similar to SLM 316L SS, the wrought sample also experiences an anodic peak and suppressed cathodic peak as a result of citrate addition to the PBS solution.

The wrought 316L SS presents almost the same trend in both PBS and citrate-PBS solutions as shown in Fig. 9b. Beyond A1, the surface is in the passive state as evidenced by the small and gradual increase in

---

**Fig. 8.** Cyclic potentiodynamic polarization in pure citrate buffer (pH 6) and Cl− containing citrate solution (pH 6 and 7.2). (a) SLM 316L SS, (b) wrought 316L SS.

**Fig. 9.** Cyclic voltammograms recorded at a scan rate of 50 mV/s in PBS and citrate-PBS for (a) SLM 316L SS, (b) wrought 316L SS.
the anodic current density. Cr$^{III}$ is the dominant oxidation state below potential 0.5 V (vs. SCE) and in PBS solution it may exist as Cr(OH)$_3.n$H$_2$O and/or Cr(OH)$_2^+$. Furthermore, the oxide/oxyhydroxides of Ni and Mo may also form within the passive film \[29\]. However, due to their relatively low concentrations within the passive film, no separate current peak was observed for these elements in the CV scans, which is consistent with other studies \[60,61\].

In contrast to the SL Malloy, the wrought alloy had an appreciable increase in current density beyond 0.4 V vs. SCE as can be seen in the inset of Fig. 9b. This rapid increase in current is attributed to the breakdown of the passive film possibly due to the transformation of Fe(OH)Cl$^+$ to FeCl$_2^{2+}$ species and by the local drop in the pH of the solution within the pit. In the presence of Cl$^-$ ions, the depletion of Cr at the vicinity of Mn/S enriched inclusions (as evident in Fig. 5b) can promote the formation of FeCl$_{aq}$ species via reaction 5 that could have deteriorated the pitting resistance of the wrought sample.

\[
\text{Fe(OH)Cl}^+ + H^+ \leftrightarrow \text{FeCl}^{2+}_{aq} + H_2O \tag{5}
\]

With the addition of citrate ions to the PBS solution, peak A$_1$ appears at relatively low potential (−395 mV SCE) and the anodic current is found to be higher than observed in PBS. At peak A$_1$, the relatively large current is attributed to the complexation of the citrate ions with the Fe$^{II}$ and Fe$^{III}$ species. The relatively large current density observed by the SLM and wrought 316L SS may enhance the dissolution of Fe in the presence of Cl$^-$ ions as discussed above.

In the case of SLM 316L SS, no abrupt increase in current is observed even at a potential higher than 0.5 V vs. SCE. This behavior corresponds to the uniform distribution of both Fe and Cr oxide/hydroxides at its surface and stability of the Cr(OH)$_3.n$H$_2$O/Cr$_2$O$_3$ even in the presence of Cl$^-$ ions. Peak A$_2$ is observed beyond 0.65 V vs. SCE, and it is associated with Cr$^{III}$ to Cr$^{VI}$ oxidation according to reaction 6 \[29,62\].

\[
\begin{align*}
\text{Cr(OH)}_3 + H_2O & \leftrightarrow \text{CrO}_2^{2-} + 5H^+ + 3e^- \\
2\text{Cr(OH)}_3 + H_2O & \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + 8H^+ + 6e^- \tag{6,7}
\end{align*}
\]

Or at pH ≤ 6.5 (which may occur inside a pit), the formation of Cr$_2$O$_7^{2-}$ may take place via reaction 7.

Peak C$_1$ and C$_2$ correspond to the reduction of high-valence Fe$^{III}$ into Fe$^{II}$ species and Cr$^{VI}$ into Cr$^{III}$ species, respectively \[63\]. During a reverse scan, the SLM 316L SS has a trace peak, C$_2$, which suggests very limited reduction of Cr$^{VI}$ to Cr$^{III}$ (reverse of reaction 6). The very small current density at peak C$_2$ suggests the greater stability of Cr$^{VI}$ species in the electrolyte that has a limited tendency to reduce to Cr$^{III}$. CV tests were also performed in citrate buffer solution (pH 6) and in Cl$^-$ containing citrate solution at both pH 6 and 7.2 as shown in Fig. 10. The CV scans for both SLM and wrought 316L SS were reversed at 0.4 V (vs. SCE) to monitor the stability of the passive film without oxidizing Cr$^{VI}$ oxide species to Cr$^{VII}$ and to evaluate the tendency of Fe$^{II}$ and Fe$^{III}$ oxide species to interact with citrate and Cl$^-$ ions. In pure citrate buffer solution, the large increase in current during anodic scans is observed for both samples and peak A$_1$ appears before approaching a limiting current (passive current density) beyond −0.2 V SCE. Comparatively, the wrought sample has a relatively large anodic current in citrate buffer solution compared to the SLM sample, which also suggests the relatively improved stability of the passive film on the SLM 316L SS. Thus, the uniform film of Cr$_2$O$_3$/Cr(OH)$_3$ on SLM 316L SS is likely
undermined on the wrought sample due to the presence of Mn/S inclusions. During the reverse scan, a very small cathodic peak C1 (compared to peak A1) is seen at −0.25 V SCE which highlights the difficulty in the reduction of FeIII and CrIII oxide species. Also, the relatively small current density observed during the reverse scan is consistent with the barrier characteristics of the formed passive film. The addition of Cl− in the citrate buffer solution (at pH 6 and 7.2) does not affect the electrochemical response of wrought 316L SS as can be observed in Fig. 10b and c. However, the anodic current density of the SLM 316L SS sample in the presence of Cl− ions is slightly increased and approaches that of the wrought 316L SS. At negative potentials (less than −0.6 V SCE), the rapid increase in the current density is attributed to the reduction of metal oxides (both Fe and Cr oxides) to elemental metals in combination with H2 evolution. Thermodynamically, the citrate ions have a strong tendency to complex with FeII, FeIII, and NiII species and these could adversely affect the barrier characteristics of the passive film [29].

Overall, the passive film formed on the SLM 316L SS sample shows extended stability within the wider potential range compared to the wrought sample (prior to the generation of peak A2 associated with the oxidation of CrIII to CrVI species). But in the case of the wrought sample, the passive film breaks down before reaching the CrIII/CrVI oxidation potential (Fig. 9b (inset)) indicating the formation of a non-homogeneous/defective passive film.

### 3.3.3. Electrochemical impedance spectroscopy

The impedance spectra (both Nyquist and Bode plots) for both alloys in PBS and citrate-PBS solutions are shown in Fig. 11. The intermediate and low-frequency regions correspond to the charge transport characteristics across the double layer and passive oxide film, respectively. The Bode phase plots show that the phase angles approach −80° within a wide range of frequency (10 to 1 Hz). The capacitive behavior of the electrical double layer and the passive film is represented as constant phase elements (CPE) (represented as Ydl and Yf, respectively) due to this shift in phase angle > −90° and this is attributed to the non-uniformity of the charge distribution across the double layer and within the passive oxide film. In other words, the Ydl and Yf are used to replace ideal capacitor behavior [64]. If the imaginary admittance of ZCPE is represented by Q, the CPE is defined as Yc, given in the following relation:

$$Z_{CPE} = Yc = \frac{1}{Q(\omega)^{a}}$$

where $\omega^2 = -1$ and represents the imaginary component of the impedance, $\omega$ is the angular frequency, a is the exponent of CPE and has a value of 0 < a < 1.

The Nyquist plots shown in Fig. 11a are incomplete semicircles with a comparatively larger imaginary impedance (−Zimg) component than the real component, Zreal. The extrapolation of these semicircles towards the low-frequency region, i.e. the intersection of the fitted curves with the Zreal axis, is used to estimate the total resistance (Rt) of the system including the electrolyte (Rs), charge transfer (Rct), and film (Rf) resistances [65]. The experimental impedance spectra are fitted by simulating the electrochemical response to an equivalent electrical circuit model (EEC), which is shown in Fig. 11b. After fitting the experimental impedance spectra, the diameter of the extrapolated semicircle of SLM and wrought alloys in PBS and citrate-PBS solutions are designated as the Rs and may be ranked in the order SLMPBS > wroughtPBS > SLMcitrate-PBS > wroughtcitrate-PBS. Thus, Rs of the SLM sample in the PBS solution are better than for the wrought sample.

![Fig. 11. Electrochemical impedance spectroscopy results showing (a) the Nyquist plots of SLM and wrought 316L SS samples in PBS and citrate-PBS, (b) the equivalent electrical circuit model used for the simulation of experimental results; Bode plots of both SLM and wrought samples in (c) PBS and (d) citrate-PBS solutions.](image-url)
The addition of citrate ions in the PBS solution results in a further decrease in the $R_c$ of both SLM and wrought samples due to the deleterious effect of citrate ions on the passive film characteristics.

Table 4 provides the quantitative information for each parameter in the EEC that is calculated through iteration of the seed values in the EEC to minimize the fitting error. The goodness of fit is estimated from the chi-squares ($\chi^2$) values that are found to be on the order of $10^{-3}$. In PBS solution, the superior corrosion resistance of the passive film of the SLM alloy is evident by the three-fold increase in $R_c$ and $R_f$ over the wrought alloy. In citrate-PBS (pH 7.2) solution, the decrease in $R_c$ from 487.0 ± 22.1 kΩ-cm² and increase in $Y_d$ (from 75.8 ± 3.1 to 103.3 ± 11.4 μS-sᵃ/㎝²) are observed for the SLM alloys, which demonstrate the negative impact of citrate ions on its corrosion resistance. A similar trend was observed for the wrought sample (from 12.1 ± 4.8 to 12.3 ± 5.2 μS-sᵃ/㎝²) which further validates the deleterious effects of citrate ions. Similar behavior of stainless steel in the presence of complexing agents has been reported by Slemnik et al. [66] and Betova et al. [67].

Though the relative decrease in $R_c$ and $R_f$ values for the SLM alloy (compared to PBS solution) is high, $R_t$ (174.6 ± 15.4 kΩ-cm²) is larger than for the wrought alloy (106.7 ± 1.9 kΩ-cm²) in citrate-PBS solution. Moreover, compared to the SLM alloy, there is a noticeable increase in $Y_f$ values for the wrought sample (from 25.6 ± 3.3 to 63.9 ± 21.0 μS-sᵃ/㎝²), which is consistent with a more defective passive film and an increase in charge transport through the double layer as predicted from the comparative increase in $Y_d$ from 103.3 ± 11.4 (SLM) to 118.3 ± 8.5 μS-sᵃ/㎝² (wrought).

The impedance spectra of both samples were also obtained in pure citrate solution with and without Cl⁻ ions at both pH 6 and 7.2 (equivalent to the Cl⁻ concentration, and pH of the PBS solution), as shown in Fig. 12. In pure citrate buffer solution, the $R_c$ of the SLM sample was larger (171.8 ± 11.2 kΩ-cm²) than the value (59.3 ± 9.9 kΩ-cm²) obtained in citrate-PBS solution. This behavior suggests that species other than citrate in the PBS solution (i.e. Cl⁻, phosphates etc.) in combination could produce aggressive conditions that may accelerate the corrosion of SLM 316L SS. A significant decrease in $R_c$ and $R_f$ in Citrate+Cl⁻ solutions at both pH 6 and 7.2 shows the significant influence of both citrate and Cl⁻ ions on the corrosion process.

In summary, the electrochemical parameters calculated from the impedance spectroscopy suggest that the SLM 316L SS offers better corrosion resistance compared to the wrought sample in the simulated biological environment investigated here, consistent with the cyclic polarization results. The better barrier characteristics of the passive film formed on the SLM 316L SS in a citrate-PBS solution that further validates the deleterious effects of citrate ions. Similar behavior of stainless steel in the presence of complexing agents has been reported by Slemnik et al. [66] and Betova et al. [67].

### Table 4

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Sample</th>
<th>$R_c$ (Ω-cm²)</th>
<th>$R_i$ (kΩ-cm²)</th>
<th>$Y_d$ (μS-sᵃ/㎝²)</th>
<th>$R_t$ (kΩ-cm²)</th>
<th>$Y_f$ (μS-sᵃ/㎝²)</th>
<th>$R_i$ (kΩ-cm²)</th>
<th>$\chi^2 / 10^{-3}$</th>
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<tbody>
<tr>
<td>PBS</td>
<td>SLM</td>
<td>16.4 ± 2.7</td>
<td>487.0 ± 22.1</td>
<td>75.8 ± 3.1</td>
<td>491.6 ± 16.3</td>
<td>13.7 ± 3.5</td>
<td>978.6 ± 14.2</td>
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<tr>
<td></td>
<td>wrought</td>
<td>16.2 ± 3.6</td>
<td>158.7 ± 15.1</td>
<td>87.2 ± 5.8</td>
<td>206.0 ± 17.2</td>
<td>25.6 ± 3.3</td>
<td>364.7 ± 3.8</td>
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<td>Citrate-PBS</td>
<td>SLM</td>
<td>12.1 ± 4.8</td>
<td>59.3 ± 9.9</td>
<td>103.3 ± 11.4</td>
<td>115.3 ± 15.5</td>
<td>68.7 ± 14.7</td>
<td>174.6 ± 15.4</td>
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<tr>
<td></td>
<td>wrought</td>
<td>12.2 ± 4.8</td>
<td>46.8 ± 13.1</td>
<td>118.3 ± 8.5</td>
<td>59.9 ± 14.9</td>
<td>163.9 ± 21.0</td>
<td>106.7 ± 1.9</td>
<td>0.61 ± 0.10</td>
</tr>
<tr>
<td>Pure citrate buffer</td>
<td>(pH 7.2)</td>
<td>21.9 ± 7.1</td>
<td>171.8 ± 11.2</td>
<td>73.0 ± 15.6</td>
<td>120.2 ± 12.5</td>
<td>55.4 ± 5.1</td>
<td>291.9 ± 17.5</td>
<td>0.63 ± 0.43</td>
</tr>
<tr>
<td></td>
<td>SLM</td>
<td>18.9 ± 6.8</td>
<td>89.5 ± 13.3</td>
<td>90.4 ± 5.7</td>
<td>159.8 ± 25.5</td>
<td>45.6 ± 5.9</td>
<td>239.4 ± 17.3</td>
<td>0.86 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>wrought</td>
<td>20.4 ± 6.0</td>
<td>146.0 ± 10.8</td>
<td>80.1 ± 20.4</td>
<td>71.2 ± 12.9</td>
<td>50.4 ± 10.7</td>
<td>217.2 ± 4.8</td>
<td>0.94 ± 0.48</td>
</tr>
<tr>
<td>Citrate+Cl⁻</td>
<td>SLM</td>
<td>17.8 ± 4.1</td>
<td>65.7 ± 6.6</td>
<td>76.6 ± 18.2</td>
<td>120.4 ± 21.6</td>
<td>89.3 ± 12.9</td>
<td>186.1 ± 15.6</td>
<td>0.92 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>wrought</td>
<td>12.3 ± 5.2</td>
<td>100.6 ± 15.4</td>
<td>112.5 ± 9.3</td>
<td>56.9 ± 9.6</td>
<td>63.9 ± 10.1</td>
<td>157.6 ± 15.7</td>
<td>0.77 ± 0.35</td>
</tr>
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</table>

Fig. 12. Nyquist plot of EIS test in citrate buffer (pH 6) and Cl⁻ containing citrate solutions (pH 6 and 7.2). (a) SLM 316L SS, (b) wrought 316L SS.
3.4. Cell proliferation experiments

Positive cell-implant interaction, such as spreading, proliferation and differentiation, is the prime requirement of innocuous biomaterials. In-vitro cell proliferation and adhesion compatibility of SLM built 316L SS and commercially available wrought 316L SS were studied to forecast the in-vivo biological response of these materials. Fig. 13 shows the fluorescence images of MC3T3-E1 pre-osteoblast cells proliferation and morphology on both of the tested materials after 48 hours of incubation. Both samples had cellular viability in terms of spreading and proliferating. However, it has been reported that besides cell viability, flattened cells with pronounced filopodia help to enhance bone formation surrounding the implant substrate [73]. Relatively higher cell concentration is clearly noticeable in the case of the SLM alloy with well-developed filopodia and supporting cytoplasmic extensions, therefore indicating healthier cell morphology and better cellular metabolism. After staining, cell densities were found to be 204 ± 3 cells/ mm² and 169 ± 2 cells/mm² on the SLM and wrought surfaces, respectively. Cell proliferation and attachment on the surface may be affected by several factors such as chemical composition, surface topology, and the rate of metallic ion release [74]. As the test was performed on the same surface condition for both samples, they should have possessed similar surface topology (and according to the EDS results their bulk chemical compositions are similar). Therefore, the amount of metallic ion released from the material might be the key factor in the noticeable differences in cell density and morphology. The toxic cations such as Ni²⁺, Cr³⁺, Mo⁶⁺ released from the SLM SS implant may induce cytotoxicity, which may ultimately cause cell death and significant morphological alteration [75]. However, the SLM 316L SS experiences lower metallic dissolution compared to wrought 316L SS as a result of improved corrosion resistance of the former as discussed above, which might limit the toxic ion release from the SLM surface. Moreover, the compact and uniform passive film resulting from refined grains and the absence of non-metallic inclusions on the SLM part impede the cationic release into the culture media. These factors promoted the suitable environment for healthier cell growth and improved proliferation on the SLM 316L SS surface. The likelihood of better cell adhesion and proliferation phenomena portrayed by the SLM 316L SS will enhance its biocompatibility for implant application.

4. Conclusions

The corrosion behavior of the SLM and wrought 316L SS was investigated in a physiological environment containing complexing agents. Pre-osteoblast cell response at the alloy surface was also measured. The corrosion properties of both of the 316L SS were greatly affected by the presence of citrate ions. Larger current densities were registered by both of the samples in citrate containing PBS solution (as opposed to PBS solution without citrate) as a result of the complexation of citrate ions with the Fe³⁺, Fe⁵⁺, and Cr³⁺ species. The refined microstructure and the absence of MnS inclusions resulted in a uniform distribution of Cr on the SLM surface, which resulted in an improved stability of the passive film as indicated by an approximately 1.5 to 2 times larger pitting resistance ($E_{\text{corr}} - E_{\text{pitting}}$), and higher protection tendency ($E_{\text{corr}} - E_{\text{pitting}}$) in biological environments compared to the wrought sample. The passive film of the SLM sample was stable up to the Cr³⁺ to Cr⁵⁺ oxidation potential. In contrast, the passive film formed on the wrought surface was not sustained until the Cr⁵⁺/Cr³⁺ oxidation potential because of the intrinsic defects in the film, which promoted accelerated localized corrosion in the form of pitting. The lower performance of the passive film on the wrought sample was attributed to the existence of Cr depleted regions across MnS inclusions. The total resistance ($R_\text{t}$) of the SLM samples was found to be approximately 1.5 to 2.5 times higher than for the wrought samples depending on the simulated environment. The high corrosion resistance of the SLM sample limited the release of toxic ions into the biological environment, which resulted in better viability and proliferation of the MC3T3-E1 pre-osteoblast cells as investigated by the in-vitro cell proliferation experiments. Overall, the additively manufactured 316L SS demonstrated superior biocompatibility in the aggressive biological environments compared to the wrought 316L SS.

Declaration of Competing Interest

The authors confirm that there is no conflict of interest regarding the work presented in this paper.

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References
